ELASTIC CONSTANTS OF POLYCRYSTALLINE VANADIUM-IRON ALLOYS

John Joseph Donegan

NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

ELASTIC CONSTANTS OF POLYCRYSTALLINE VANADIUM-IRON ALLOYS

by

John Joseph Donegan Jr.

Thesis Advisor: J. R. Neighbours
E. C. Crittenden Jr.

September 1972

Approved for public release; distribution unlimited.

Elastic Constants of Polycrystalline
Vanadium-Iron Alloys

by

John Joseph Donegan, Jr.
Lieutenant Commander, United States Navy
B.S., United States Naval Academy 1963

Submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

from the
NAVAL POSTGRADUATE SCHOOL
September 1972

ABSTRACT

Polycrystalline alloys of iron in vanadium up to 15.32 atomic percent were prepared principally by arc melting. In order to obtain the elastic constants and investigate the possibility of the existence of an elastically isotropic alloy ultrasonic measurements were made. These measurements determined the longitudinal and transverse wave velocities in the 10-30 MHz range at room temperature. The resulting longitudinal modulus increased with alloying whereas the shear modulus remained roughly constant although the data are somewhat scattered. These data are interpreted to show that the shear constants vary through alloying in a manner consistent with the results of other experiments and that the results are consistent with a $s^1 d^{n+1}$ electronic configuration in the transition metals. The existence of an isotropic alloy is indicated for alloys with electron to atom ratios lower than vanadium rather than for the alloys measured.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

The author wishes to acknowledge the Bureau of Mines for providing most of the vanadium. Also Dr. Martin Glicksman and his group at the Naval Research Laboratory are thanked for their assistance in preparation of the alloys. Finally much gratitude is owed to John R. Neighbours and Eugene C. Crittenden, Jr., Professors of Physics, Naval Postgraduate School whose guidance made this work possible.

I. INTRODUCTION

The decision to investigate the elastic properties of a vanadium-iron alloy was the result of a desire to have an elastically isotropic material such as tungsten, but without tungsten's high melting point, for use in a thin film experiment. It was felt that the isotropic property of such a material would also be advantageous in macroscopic polycrystalline form. Isotropic grains would tend to deform uniformly in the presence of an overall stress irregardless of their orientations. This effect would reduce one source of motion at the grain boundaries resulting in a corresponding improved resistence to cyclic fatigue.

It was known that the ratio of the elastic shear moduli, A = C/C', called the Zener anisotropy is less than unity for some of the bcc transition elements and greater than unity for others. Using a simple Vegards's Law model for the variation of A with alloying, various phase diagrams were investigated to find a pair of constituents where the required relative concentrations for isotropy fell in a region of solid solubility of the system. The vanadium-iron system was found to have a solid solution bcc phase up to approximately 40 at.% iron in vanadium. On the basis of Vegard's Law the concentration of iron for isotropy was estimated to be approximately 12 at.%. Another influencing factor in the choice of the V-Fe system was the recent availability of very high purity vanadium.

The free atom electron configuration of vanadium is $4s^2 3d^3$ and of iron, $4s^2 3d^6$. Thus the addition of iron to vanadium increases the electron to atom ratio of the alloy. According to Fuchs [Ref. 1] the resistance to shear in metals is a result of two interactions: (a) the Coulomb attraction between positive ions and negative conduction electrons, and (b) the exchange interaction between ions, thought to be significant only between nearest and second nearest neighbors. This second interaction depends in a sensitive way on the electron configuration and, in transition metal alloys in particular, the d shell electrons are thought to contribute significantly.

Very little work has been done on the elastic constants of binary alloys where both constituents are transition metals. In addition to making an isotropic alloy some knowledge about the interaction between atoms in such an alloy would be expected to be gained from the analysis of a series of compositions. Therefore, seven polycrystalline compositions of the vanadium-iron system were produced with iron content between 3.25 and 15.32 at.%. The longitudinal and transverse elastic constants were determined, by a pulse echo method, for each composition. Then, using an empirical relation for the shear constant $C' = 1/2(C_{11} - C_{12})$, the single crystal elastic constants were calculated and discussed in light of the variations in electron to atom ratio and the d-band contributions.

The classical theory of elasticity is discussed in Appendix I and the Fuch's theory of determination of the

elastic constants from fundamental considerations is discussed in Appendix II.

II. EXPERIMENTAL DETAILS

A. SAMPLE PREPARATION

The preparation of the seven alloys used in this study was done at the Naval Research Laboratory, Washington, D.C. The history of each sample measured is shown in Table I. Commercial analysis of the composition and impurities of each sample is shown in Table II.

Two methods of producing the alloy were used. The constituents were melted by an electron beam in vacuum or arc-melting under an ultra-pure helium atmosphere. Electron beam melting was discontinued after the second sample when it was determined that the refining effect of this method reduced the iron content of the alloy by unpredictable amounts. Ingots from both methods were hot forged and swaged into rods. A typical rod was 3/8 to 1/2 inch in diameter and 12 to 15 inches long.

These rods were used in attempts to grow alloy single crystals. The attempted growth methods were liquid float zoning and strain annealing. All of the samples exhibited grain growth: zone melting produced grains of .25 to .75 mm diameter, while strain anneal methods produced grains of 1.25 to 3.75 mm diameter. Time and the availability of material precluded a more thorough exploration of the possibilities of producing single crystals and thus polycrystalline rods of each composition were selected for measurement.

Fourteen specimens were made from the seven alloys. Seven were 2 cm long and .635 cm in diameter. These were used for measuring the longitudinal velocity. The remainder, cut adjacent to the first, were 1 cm long and were used for measuring the transverse velocity. To provide the best possible diameter to wavelength ratio in the transverse samples the largest available diameter was preserved in each case. Sample diameters varied from .635 cm to 1.10 cm. The ends of all of the cylindrical specimens were machined flat and parallel and the surface polished. The surfaces were found to be parallel to an average of 1.5 milliradians.

B. MEASUREMENT OF THE SOUND VELOCITY

The velocity of sound in the seven alloys was measured by the pulse echo technique. A sound pulse was transmitted into the material by a piezo-electric quartz transducer driven by a pulse generator operating at the transducer fundamental frequency or an odd harmonic. The initial pulse and each succeeding echo can be received by a second transducer. This second transducer is placed at the opposite end of the sample. For the transverse measurement the two transducers must be aligned so that their particle motions are parallel. The two transducer method eliminated saturation of the receiver amplifier by the driving pulse. The arrival time of each echo is usually determined by using an oscilloscope trace with a delay time multiplier.

The transducers used were 10MHz X cut quartz for the longitudinal mode measurements and AC cuts of the same frequency for the transverse mode. The transducers were bonded to the samples with Salol. A spring loaded jig was used so that both transducers could be bonded simultaneously. This improved the uniformity of the bonds and eliminated the problem of melting the first bond while the sample was being heated for the second. During the measurements the sample was suspended at its center by a three point circular holder which was concentric with two shielded contacts spring loaded to the transducers. Series coils were employed to provide a low impedance match of the capacitive transducers to the pulse generator and receiver. All measurements were performed at ambient room temperature (294 K).

The alloys in this experiment were, in most cases, highly attenuating. The transverse mode was generally more attenuated than the longitudinal mode and often only two or three echos could be discerned above the system noise. Measurements of the total attenuation were made in the longitudinal case. The total attenuation includes all loses, which are loses at the bonds and transducers as well as in the sample themselves. These loses varied from a low of 3db per cm for the best sample to approximately 5 db per cm for the worst sample. For this reason the unrectified pulse waveform, after amplification, was further processed by a

Princeton Applied Research (PAR) Model 160 Boxcar Integrator.

The boxcar integrator has three principal advantages for the pulse echo experiment. It provides a large improvement in signal to noise ratio. It faithfully reproduces the small amplitude portions of the waveform so that the arrival time of the pulse can be accurately determined. In conjunction with a strip chart recorder it provides a permanent working data record. The boxcar integrator operates by scanning an aperture in time along the waveform and averaging the value of the signal at each point over many repititions of the waveform. The result is that the random noise fluctuations on the signal will average to zero, and if enough repetitions of the signal are integrated, the output will be the true value. Typically 50 usec of the echo train was scanned using a 10 nsec aperture. Such an aperture can resolve frequencies up to about 30 MHz. The scanning time to make each pass along the train was 50 minutes. A pulse repitition frequency of 10 KHz was used so that each point on the waveform was sampled $6x10^3$ times. The output to the strip recorder is then a picture of the echo train produced at one microsecond per minute. By diverting the boxcar input to the time mark generator that was triggering the experiment a trace of convenient time marks could be placed in the "dead space" between echos. These time marks could not be used to measure the arrival time of echos, however, since any variation in the linearity of the travel of the aperture

along the signal (ie along the timebase) or any variation of the speed of the strip chart recorder would have the effect of expanding or contracting the trace. Instead the voltage corresponding to the position of the aperture along the timebase was used to drive a second pen which ran concurrently with the echo trace. (Figure 1) This second trace was used to determine the echo arrival times. The accuracy of the time measurement is improved by this refinement since if the nonlinearities above occur they will be automatically compensated. The time marks on the echo trace were used to check the calibration of the time trace. Electronic instability over the relatively long times required to make a trace did not present a problem. Variations in the trigger rate of the time mark generator or in the trigger response of the pulse generator and boxcar integrator that would have resulted in noise in the output trace were not observed to occur. From these traces the arrival time of each echo was measured and plotted against the elapsed path length. The slope of this plot is the sound velocity.

In a homogeneous polycrystalline material the value of the transverse velocity should not depend on the orientation of the transducer with respect to the sample. Such is not the case in single crystal measurements where alignment of the particle motion with certain crystallographic directions is required to determine the elastic constants. The rather large grain size in these samples could have the effect that

the orientations of the grains might not be sufficiently random to result in the true average velocity being measured. This effect of a lack of randomness is reduced if the anisotropy of the individual grains is low, and vice versa. To compensate for any lack of random grain orientation velocity measurements were made on each sample with the induced particle motion oriented at 0, 60 and 120 degrees from an arbitrary mark. The velocities thus measured and several values at unknown orientations were combined by taking the arithmetic mean as the velocity for the composition. The choice of a difference in angle of $\Pi/_3$ for the various orientations was chosen as convenient and because a cubic material has $\Pi/_4$ symmetry. The variation of sound velocity with orientation for each sample is indicated by the bars on the data in Figure 4. These bars are drawn between the maximum and minimum velocities observed. The average variation in velocity between orientations and samples was 2.26%. The repeatability on a given sample for a given orientation is within the accuracy of the experiment which is discussed below.

To determine the elastic constants both the sound velocity and the density of the sample must be known. Pearson [Ref. 2] lists data by Hanneman and Mariano which includes the value of the lattice parameter of the vanadium-iron system for 0, 9.5 and 20.5 at.% iron. If a smooth curve is drawn through these points the lattice parameter of the seven alloy compositions used can be found. The density

determined by this method is compared in Figure 2 with the density determined by weighing and measuring the samples. Figure 2 shows density as a function of the atomic percentage of iron and indicates the agreement between the two methods is within 1% for all compositions. The experimental points can also be fitted to a straight line with one point outside of 1% and an average deviation of 0.3%. Such a straight line fit would increase the density determination of the dilute composition approximately 0.5% and decrease the concentrated composition a like amount. It is felt that the precision of the x-ray determination of the lattice parameter exceeded that of the experimental check on the calculated density so that the density of each composition has been calculated from the lattice parameter read from a smooth curve through the published values.

III. EXPERIMENTAL RESULTS

The elastic constants of a cubic polycrystalline material are the shear constant G, and the longitudinal constant, $(B + \frac{4}{3} G)$, where B is the bulk modulus. Appendix I shows that the longitudinal and transverse sound velocities are given by

$$V_L = \sqrt{\frac{B + \frac{4}{3} G}{\rho}} \qquad V_S = \sqrt{\frac{G}{\rho}}$$

In order to compare the quantities measured for the alloys with those of pure vanadium the Hill method [Ref. 3] was used to average over all lattice orientations the single crystal elastic constants of vanadium as measured by Alers [Ref. 4]. This average is required to obtain the polycrystalline value of G and is also discussed below. The bulk modulus in cubic materials is the same for the single crystal and polycrystal case. After a small correction for the difference between the density used by Alers and that calculated from the lattice parameter B and G for pure vanadium are known. For vanadium and each composition, the atomic percentage of iron, density, longitudinal constant, shear constant and bulk modulus are given in Table III. Graphs of the measured elastic constants which also contain the calculated values for vanadium are shown in Figure 3 to Figure 5.

The longitudinal modulus (Figure 3) increases with increasing iron concentration. The experimental data is fitted best by a least squares parabola. With the exception of the 3.25 at.% composition, which is approximately 2% low, all of the other samples and the vanadium value fall within 1% of this fit. Above approximately 5 at.% iron the measured values increase essentially linearly. However, a linear least squares fit to the data had a larger least square error and fell approximately 3% low for the value of pure vanadium.

The transverse modulus (Figure 4) is essentially constant over the entire range of compositions investigated. These is considerably more scatter in the data for the transverse case than in the longitudinal case. The best fit straight line increases approximately 1.5% over the pure vanadium value for the 15.32 at.% composition. All of the samples fall within 5% of this line with the exception of the 7.40 at.% composition which is approximately 12% low. The reproducibility of this low velocity for sample 3 was demonstrated on a third specimen cut adjacent to the first two. Because of the small size of the transverse constant with respect to the longitudinal constant the percentage errors are larger although the absolute errors are approximately the same.

The bulk modulus (Figure 5) is readily obtained from the definition of the longitudinal constant $(B + \frac{4}{3} G)$. Since it is a combination of both the longitudinal and

transverse constants it reflects both the rise with increasing iron concentration of the longitudinal constant and the scatter present in the transverse data.

Based on the estimate of the errors in the measured time, length and density the accuracy of a single measurement of ρV^2 is estimated to be approximately .75%. The largest portion of this error is in the time determination. Differences in individual echo arrival times for different runs on the same sample that resulted in the same velocity were found to be approximately .75%.

IV. DISCUSSION

The two elastic constants measured in a polycrystalline experiment are the shear constant, G, and the longitudinal constant $(B + \frac{4}{3} G)$. For this experiment therefore the experimental results are the variation of the shear modulus, G, and the bulk modulus, B, with increasing atomic percentages of iron.

Although the interpretation of these results alone is interesting they do not provide as much information, that would be useful in interpreting the fundamental contributions of atomic forces to the elastic constants, as the single crystal elastic constants would. (See Appendix II for the theory of the fundamental contributions to elastic constants) Moreover, for cubic materials there are three non-zero independent elastic constants, (See Appendix I) and it is impossible to unfold these three quantities from the two measured quantities.

An independent source of the third constant was available in the work of Fisher and Dever on the stability of bcc transition metals [Ref. 5]. They present an empirical relation for the C' elastic shear constant as a function of the electron to atom ratio of transition metal alloys. Here C' is one of a set of 3 constants which are linear combinations of the basic cubic constants, C_{11} C_{12} and C_{44} (See equation A1.8, f.f.).

$$B = \frac{C_{11} + 2C_{12}}{3}$$

$$C' = \frac{C_{11} - C_{12}}{2} \qquad (1)$$

$$C = C_{44}$$

Here B is the bulk modulus and C and C' are shear constants. In terms of this set of constants the measured bulk modulus for the polycrystalline material is directly comparable with $B=1/3(C_{11}+2C_{12})$, however, the shear modulus, G, is a function of both C and C'. The fact that G is a known function of C and C' is a result of the methods of determining polycrystalline aggregate moduli, as averages of the single crystal moduli. It is thus instructive to digress briefly to discuss these averages.

In 1952 Hill [Ref. 3] showed that two classical approximation to polycrystalline averages by Voigt in 1928 [Ref. 6] and Reuss in 1929 [Ref. 7] were upper and lower bounds on the problem and suggested the arithmetic mean as an average that would be closer to measured values. Voigt averaged over all lattice orientations using the assumption that the strain is uniform throughout a grain. Reuss did the averaging assuming that the stress is uniform throughout a grain. Following Hill, the strain energy function of an isotropic material in terms of the principal stresses T_i and strains e_j and the unknown bulk and shear modulus, B and G are

$$w = B(e_1+e_2+e_3)^2 + \frac{2}{3}G \sum_{i\neq j=1}^{3} (e_i-e_j)^2 \qquad (2)$$

$$w = \frac{1}{B}(T_1+T_2+T_3)^2 + \frac{3}{2G} \sum_{i\neq j=1}^{3} (T_i-T_j)^2 \qquad (3)$$

Even though the Voigt and Reuss approximation are limits they lead to simplified relations between the polycrystalline constants and the single crystal constants.

$$9B_v = (C_{11}+C_{22}+C_{33}) + 2(C_{12}+C_{23}+C_{31}) \qquad (4)$$

$$15G_v = (C_{11}+C_{22}+C_{33}) - (C_{12}+C_{23}+C_{31}) + 3\ (C_{44}+C_{55}+C_{66}) \qquad (5)$$

$$\frac{1}{B_r} = (S_{11}+S_{22}+S_{33}) + 2(S_{12}+S_{23}+S_{31}) \qquad (6)$$

$$\frac{15}{G_r} = (S_{11}+S_{22}+S_{33}) - 4(S_{12}+S_{23}+S_{31}) + 3\ (S_{44}+S_{55}+S_{66}) \qquad (7)$$

These relations apply to all crystal classes and the subscripts v and r deonte Voigt and Reuss respectively. The S_{ij} are the elastic compliances (see Appendix I).

By writing the C_{ij} or S_{ij} in (4) through (7) in terms of the cubic constants C_{11}, C_{12} or C_{44} and using the cubic inverse relations

$$C_{44} = \frac{1}{S_{44}},\quad (C_{11}-C_{12}) = \frac{1}{(S_{11}-S_{12})},\quad (C_{11}+2C_{12}) = \frac{1}{(S_{11}+2S_{12})}$$

one obtains,

$$B_v = B_r = \frac{1}{3}\ (C_{11}+2C_{12}). \qquad (8)$$

which is identical to the single crystal experssion in equation (1), and

$$G_v = \frac{1}{5}(C_{11}-C_{12}+3C_{44}) \qquad G_r = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}-3(C_{11}-C_{12})} . \qquad (9)$$

Now converting to C and C' using equation (1)

$$G_v = \frac{2}{5}C' + \frac{3}{5}C \qquad G_r = \frac{10CC'}{4C + 6C'} . \qquad (10)$$

The Hill average of these $G = 1/2\ (G_v + G_r)$ is

$$G = \frac{1.2[C+C']^2 + 5.2CC'}{4C + 6C'} . \qquad (11)$$

Equation (11) is the desired expression for the shear constant in terms of C and C'.

Returning now to the empirical relation of Fisher and Dever for the shear constant C',

$$C' = 0.01391 \times 10^{12}\ (e^*/a)^{3.34} \text{dyne/cm}^2 . \qquad (12)$$

This power law relation for C' was determined by taking the best fit of values of C' for three Ti-Cr alloys and the published values of C' of vanadium and chromium. In this fit the electron to atom ratio was a parameter. The details will be considered below. The central result was that by assigning effective electron to atom ratios, e*/a, of 2, 3, and 4 to titanium, vanadium and chromium respectively they could obtain the relation (12).

Two important questions can be raised. First why does C' seem to depend more on an electron to atom ratio, than

on the electrostatic and ionic contributions to the shear constants outlined in Appendix II. Second, why the particular numbers 2,3,4 instead of the total valency or some other number. Quantitative answers are not forthcoming, however qualitatively the reasoning is as follows. If in the region of (e*/a) from 2.15 to 4.0, C' is governed by the relation (12) (the e*/a range of the present work is from 3.0 to 3.46) then a relation of the same form and similar magnitude should exist for the 4d and 5d transition metals, Nb, Ta, Mo and W. By plotting the published values of C C' and C_{11} versus e*/a for V, Nb, Ta, Cr, Mo, and W and looking at the percentage variations between the 3d, 4d and 5d elements they conclude that although C' does not depend entirely on e*/a it has much more of this type dependence than do C_{11} or C. They speculate that d electron exchange interaction with nearest neighbors could overcome the negative contribution of ionic overlap discussed in Appendix II.

For the choice of e*/a of 2,3 and 4 for titanium, vanadium and chromium respectively Fisher and Dever refer to a recent APW band calculation of the transition elements by Snow and Waber [Ref. 8]. In this calculation, Snow and Waber compute the electron occupancy of the s, p and d bands as well as the number of electrons in the external region between the atomic spheres that are characteristic of the APW method. These occupancies are computed for two initial configurations of electrons, s^1d^{n+1} and s^2d^n where

n varies from 2 for titanium to 9 for copper. Snow and Waber favor the s^1d^{n+1} configuration as the most probable and, for this configuration, show d shell occupancies of 2.11, 3.07 and 4.01 for titanium, vanadium and chromium respectively. These are very close to n which is the e*/a chosen by Fisher and Dever for the same elements. Thus if the d shell interactions are considered the primary contribution to C' this seems to be reasonably good evidence for the chosen values of e*/a.

For the vanadium-iron alloy of this work the e*/a of the seven compositions could be computed using the value of 3.0 for vanadium and by referring to Snow and Waber's work choosing the ratio 6.0 for iron. They give a d shell occupancy of 6.18 for iron starting from the s^1d^{n+1} configuration. Then using equation (12) C' could be computed for each composition. These values of C' and the measured values of G can then be used to solve equation (11), for the shear constant C of each composition. These results are listed in Table III along with the best fit values of the derived quantities.

In Figure 6 is shown the results of all the known shear constant data for the bcc region of the first period transition elements and their alloys. The values of C and C' shown for vanadium-iron region are speculative in that they are derived from an empirical data fit and a polycrystalline experiment. However, the derived values of C in the region e*/a = 3.0 to 3.46 are continuous with the results of the

Fisher and Dever alloy experiment which are in the region e*/a = 2.15 to 2.6 of the figure. The only other known experiment in this region is the work on molybdenum-rhenium by Davidson and Brotzen [Ref. 9] which is shown in the region e*/a = 4.0 to 4.26 of the figure. Fisher and Dever had no explanation for how the values of C for vanadium and chromium joined up. These results of the present work merely state that C decreases before increasing to the chromium value. The scatter in the C values reflects the scatter in the experimental results. The points for V-Fe alloys on the C' line in Figure 6 are calculated from the empirical relation (12) and it can be seen that C' apparently has a maximum at e*/a = 4.0. Fisher and Dever point out that this maximum corresponds to the maximum d band width in Snow and Wabers calculation.

Variation in the anisotropy ratio with e*/a is readily apparent in Figure 6. At the left hand side the ratio is greater than unity and decreases to that value for e*/a of 2.8. It continues to decrease through the V-Fe region. In the region above e*/a = 4 the anisotropy is again increasing for the Mo-Re alloys. The anisotropy returns to unity for e*/a = 4.26. Thus the concept of an isotropic V-Fe alloy is probably incorrect. A more likely choice would be vanadium with a few atomic percent titanium to make e*/a = 2.8. Ti-V forms a bcc solid solution in this region.

It is interesting to note in Figure 6 that C extrapolates to zero at an e*/a of approximately 4.2 which also heralds the onset of the sigma phase of the vanadium-iron system [Ref. 10]. That C would continue to zero and create an instability seems unlikely and it is thus assumed that C must increase eventually toward the Cr value. In terms of the energy of an electron gas discussed in Appendix II, the addition of electrons in the region above e*/a=3.5 would push the Fermi surface closer to the Brillouin zone boundary where shear strain on the direct lattice, which is, of course, reflected in the reciprocal lattice could increase the average electron kinetic energy and contribute a positive component to C. Another way of visualizing the electron gas effect on C is in terms of the density of states function. Snow and Waber show that the density of states at the Fermi level varies with group number in such a way that a minimum occurs for e*/a just less than 4 for the s^1d^{n+1} configuration. This is the region where increasing e*/a causes the Fermi level to traverse between the lower energy bonding states of the d band and the upper energy anti-bonding states. The correlation between these effects and the requirement that the C value reach a minimum and turn up toward chromium is unknown. It is only pointed out that they both occur in the same region of e*/a. This concludes the discussion of the shear constants. Before going on to the bulk modulus a short discussion of how the various ratios, e*/a, were determined is included.

In making the choice of e*/a for the elements, Fisher and Dever plotted C' for their three alloy compositions, vanadium and chromium versus 1, 2, 3 and 4 excess electrons in chromium over those in titanium. Only the value 2 gave a smooth curve through the five points. They then plotted ln C' versus ln e*/a for and e*/a of Cr from 1 to 8. The only e*/a to come within the experimental error of C' for their alloy and V was e*/a = 4 for chromium. This fit was 1.25% low for the published C' of Cr. and had the parameters given in (12).

Since they had established the e*/a for V the remaining choice in this work was the value for Fe. Values of C were calculated using e*/a = 6 and 7 for iron. An e*/a of 7 has the effect of increasing the maximum e*/a for V-Fe to 3.61 and slightly lowers the C values. However, since G is very insensitive to change in e*/a a choice between 6 and 7 could not be made on this basis and it was decided to be consistent and use the s^1d^{n+1} configuration with an e*/a of 6 for iron. If possible errors in the determination of G are considered it is found that even if G were to increase with alloying at the same rate as the longitudinal constant the physical result that C decreases with alloying for e*/a above 3.0 would only be changed in degree.

Published values of the bulk modulus in the transition metals [Ref. 11] show that it is peaked in each long period in the vicinity of Group VIIIB. This dependence is similar to that of the cohesive energy and is independent of an

interpretation of any model of the contributions to the bulk modulus. Converting to electron concentration, as has been discussed above, these data and other published results for alloys support the idea that the bulk modulus increases with increasing electron concentration up to a maximum at e*/a of 4 or 5.

One may think of the bulk modulus as arising from the "free" electron gas and from the ion-ion interactions. Snow and Waber using the s^1d^{n+1} configuration estimate that the s like portion together with the charge external to the atomic sphere is between 1.0 and 1.5 electrons. In the alloys investigated here the lattice shrinks with the addition of solute. This means that if only these electrons are considered as contributing to the bulk modulus it will increase with decreasing lattice parameter. A simple estimate shows that this contribution is about 30% of the total for pure vanadium and roughly the same fraction for the alloys. Thus one may infer that both contributions increase with alloying. Then for the ionic contribution one may conclude that alloying iron with vanadium increases the bulk modulus either because the iron-vanadium ion interactions are larger or because the iron-iron interactions are larger. From the shape of the bulk modulus curve the latter interpretation seems more probable.

V. CONCLUSIONS

Addition of iron to vanadium increases the bulk modulus but not the shear modulus, although the latter data are scattered. The increase in the bulk modulus can be partially attributed to an increase in electron gas concentration and partially attributed to an increase in ion-ion interactions. The relative contributions of the s and "free" electrons through the electron gas and ion-ion exchange interaction is approximately constant for the range of alloys studied.

Since the shear modulus remains constant this means that the shear constants C and C' do not change with alloying or more probably that they each change at different rates. Using the empirical relation of Fisher and Dever for C' the variation of both shear constants with electron concentration is consistent with the previously measured values for vanadium and the titanium-chromium alloys.

The anisotropy ratio is a smoothly varying function over the range of effective electron concentrations from 2 to 4.5. Thus this work supports the idea of an s^1d^{n+1} configuration for the transition metals and an almost complete dependence of C' on the electron to atom ratio. The concept of an isotropic alloy of the transition elements has been demonstrated in the Mo-Re case. The existence of a second such alloy between two first long period elements, V-Ti, is indicated.

Future work in this area could include investigation of the elastic constants of a series of various alloys with e*/a from 2.15 to 4.30. Such alloys as V-Ti, V-Cr, V-Fe and Cr-Fe might be employed to investigate this entire region of bcc stability in the transition elements.

TABLE I

No.	Production technique	Vanadium source	Crystal growth and anneal technique
1.	arc melting	Argonne National Laboratory	annealed 1 1/2 hours at 1000C longitudinal and transverse velocity were measured annealed 4 hours at 1600C
2	electron beam melting	Bureau of Mines electrolytically refined	float zone melting
3	arc melting	Bureau of Mines vacuum arc melted	strain anneal annealed 2 1/2 hours at 1600C swedged to strain annealed 1 1/2 hours at 1600C
4	arc melting	Bureau of Mines electrolytically refined	passed slowly through an induction coil after straining this took 4 hours at 1600C
5	electron beam melting	Naval Research Laboratory	float zone melting
6	arc melting	Argonne National Laboratory	same as sample 1
7	arc melting	Bureau of Mines electrolytically refined	float zone melting

Notes

1. Iron for all samples was produced at NRL [Ref. 12]

2. Vanadium produced by the Bureau of Mines is reported in [Ref. 13 and 14].

3. All anneals were done in vacuum

4. Temperatures during anneals were determined by optical pyrometry.

TABLE II

Atomic percent

No.	V	Fe	Cu	Al	Cr	O	H	N
1	96.51	3.25	0.1206	nil	0.0098	0.0926	0.0152	0.0073
2	94.59	5.35	nil	nil	0.0049	0.0288	0.0254	0.0037
3	92.37	7.40	nil	nil	0.0335	0.1475	0.0356	0.0110
4	88.94	10.96	0.0033	nil	0.0075	0.0482	0.0357	0.0037
5	92.55	7.24	nil	0.0304	0.0022	0.1313	0.0356	0.0073
6	85.95	13.94	0.0130	nil	0.0149	0.0484	0.0256	0.0111
7	84.59	15.32	nil	nil	0.0060	0.0291	0.0462	0.0074

Carbon	all samples under .005 wt.%
Sulfur	all samples under .005 wt.%
Phosphorus	all samples under .005 wt.%

Analysis performed by Kennard and Drake Co., Los Angeles, Cal.

TABLE III

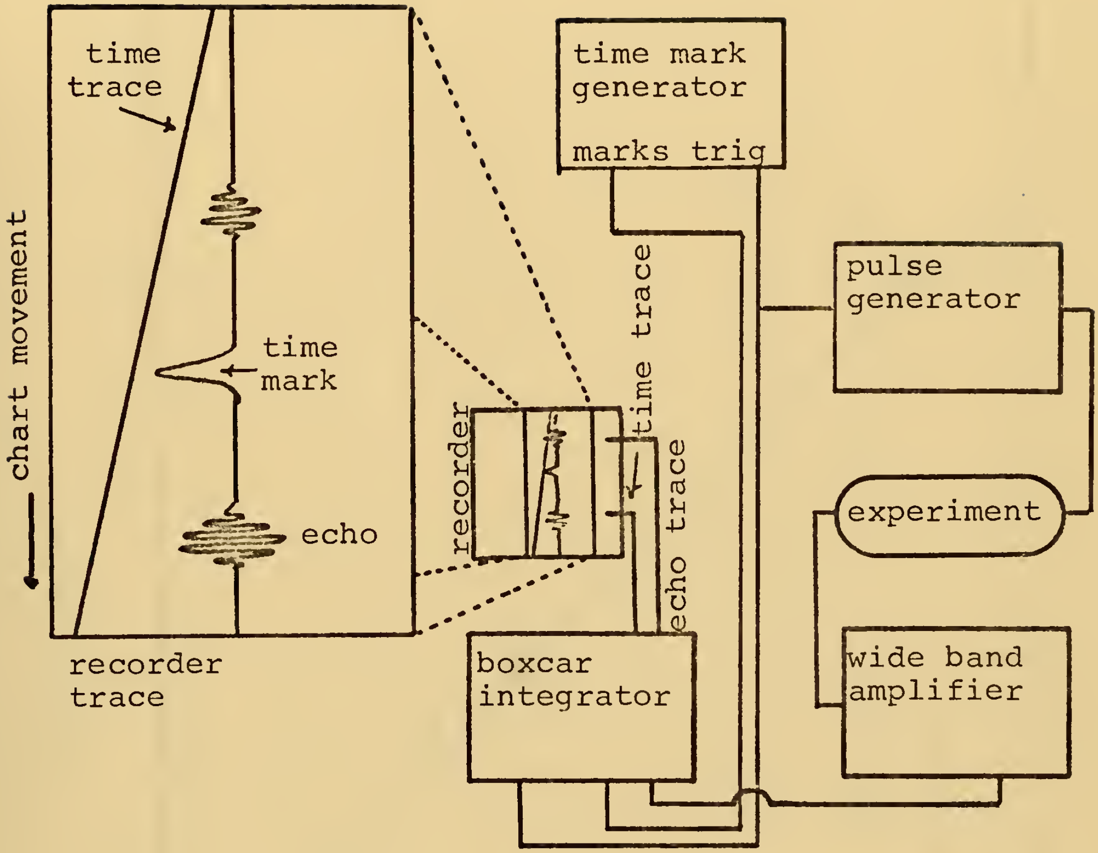
No.	Fe%	ρ	$[B+\frac{4}{3}G]$	G	e*/a	C'	C	B	A
V	0.00	6.0699	2.196	0.474	3.00	0.546	0.431	1.564	0.79
1	3.25	6.1809	2.151	0.480	3.10	0.609	0.410	1.511	0.67
2	5.35	6.2438	2.230	0.452	3.16	0.649	0.353	1.628	0.54
5	7.24	6.2969	2.236	0.490	3.22	0.691	0.388	1.583	0.56
3	7.40	6.3017	2.250	0.415	3.22	0.691	0.291	1.696	0.42
4	10.96	6.3916	2.284	0.479	3.33	0.773	0.344	1.645	0.45
6	13.94	6.4609	2.376	0.483	3.42	0.845	0.326	1.731	0.39
7	15.32	6.4917	2.401	0.469	3.46	0.879	0.300	1.776	0.34

calculated best fit values

No.					e*/a	C'	C	B	A
V					3.00	0.546	0.415	1.565	0.76
1					3.10	0.609	0.388	1.573	0.64
2					3.16	0.649	0.372	1.588	0.57
5					3.22	0.691	0.357	1.611	0.52
3					3.22	0.691	0.357	1.611	0.52
4					3.33	0.773	0.331	1.672	0.43
6					3.42	0.845	0.310	1.742	0.37
7					3.46	0.879	0.301	1.778	0.34

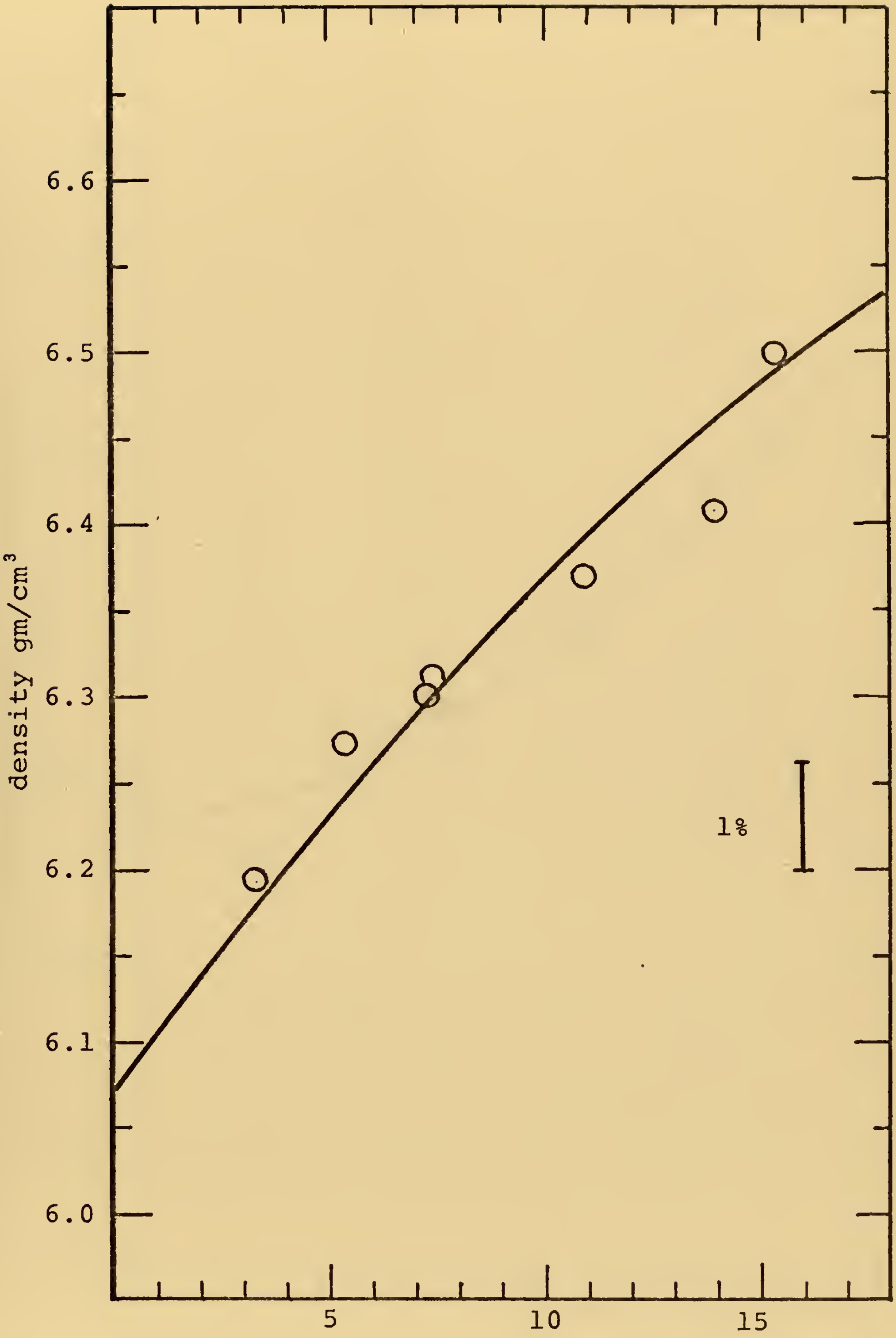
ρ in gm/cm^3

$[B+\frac{4}{3}G]$, G, C, C', B in $10^{12} dyne/cm^2$



Equipment schematic

Figure 1



atomic percent iron

Figure 2

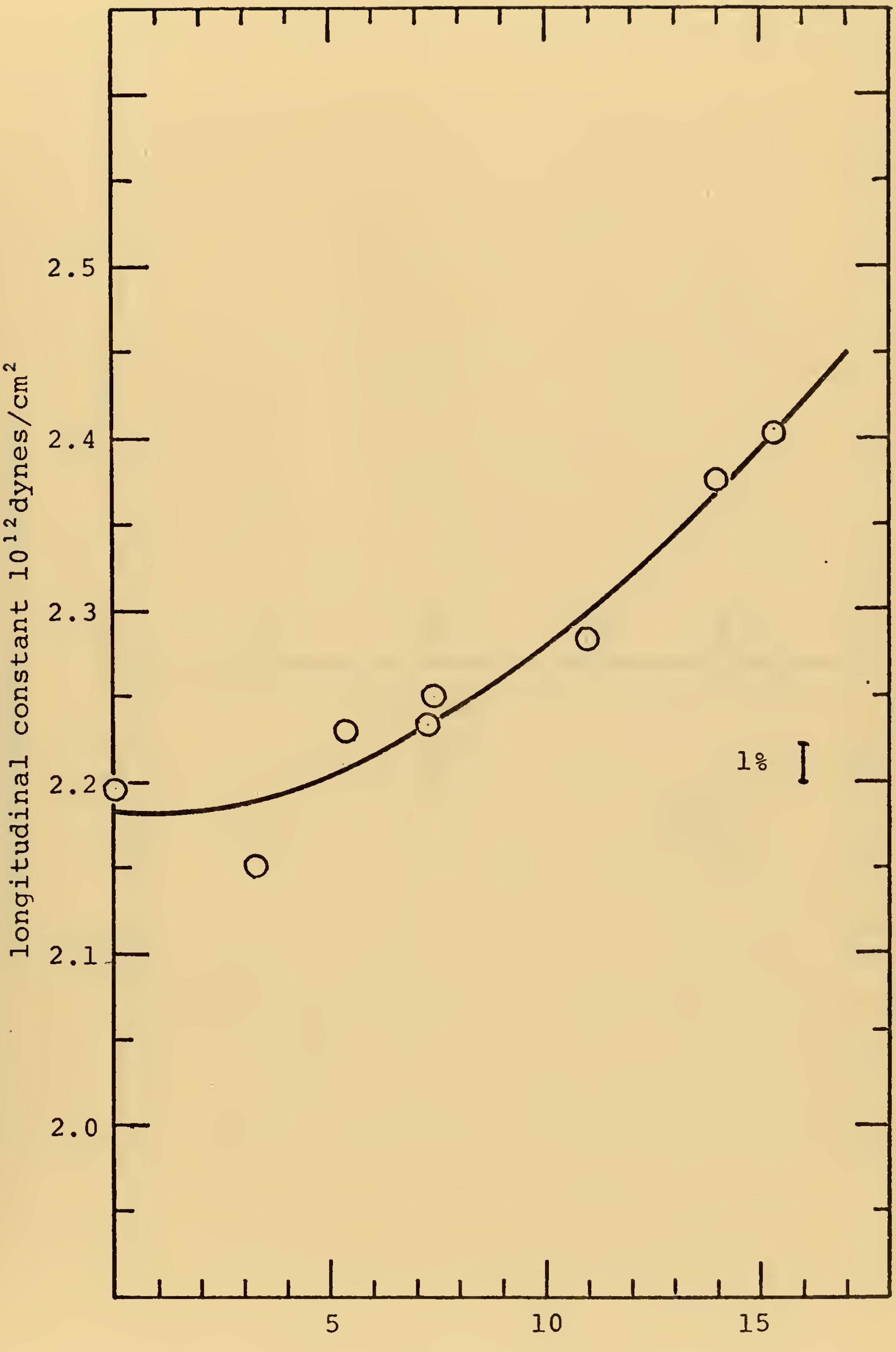

longitudinal constant 10^{12} dynes/cm^2
2.5
2.4
2.3
2.2
2.1
2.0
1%
5
10
15
atomic percent iron

Figure 3

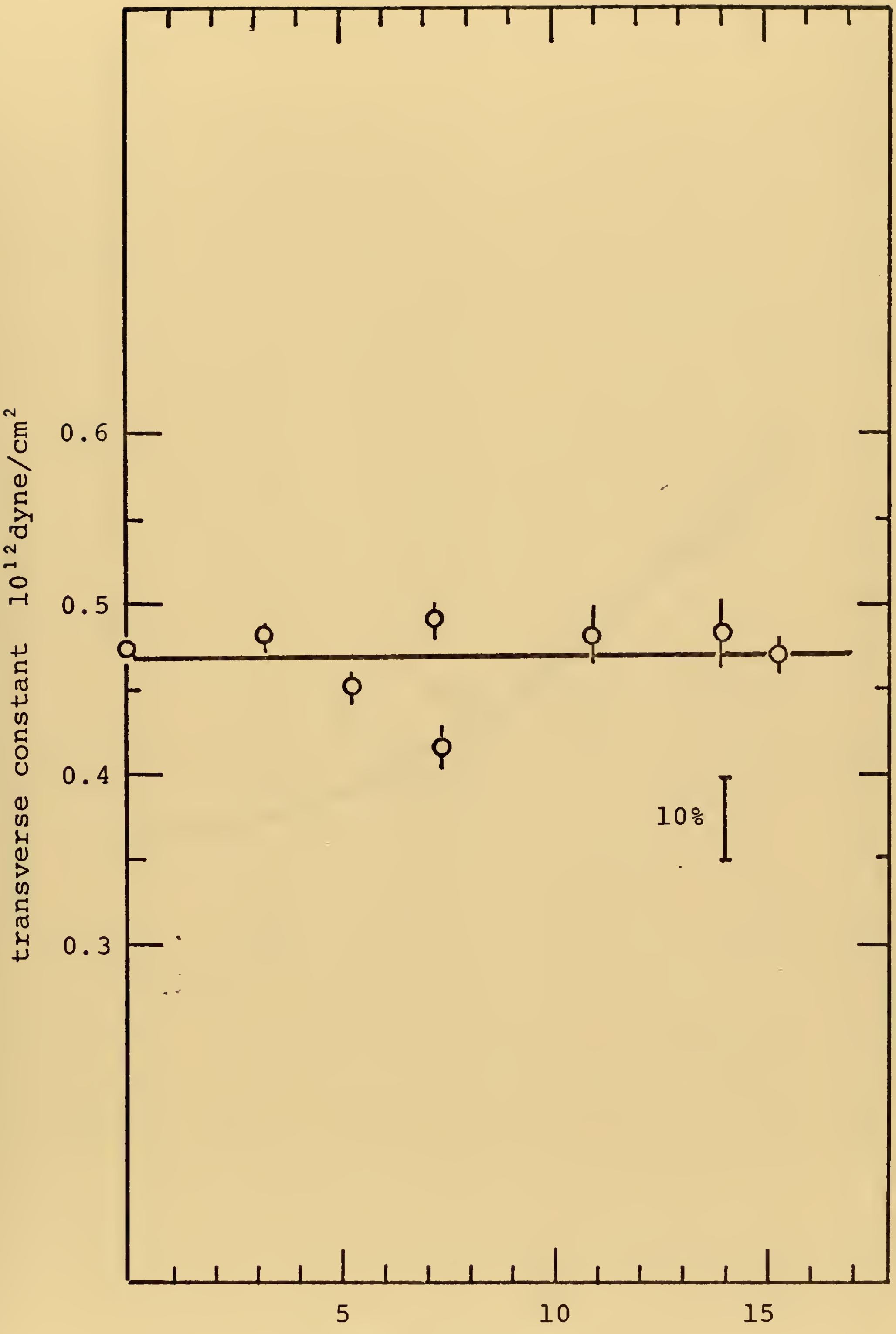

transverse constant 10^{12}dyne/cm^2
0.6
0.5
0.4
0.3
10%
5
10
15
atomic percent iron

Figure 4

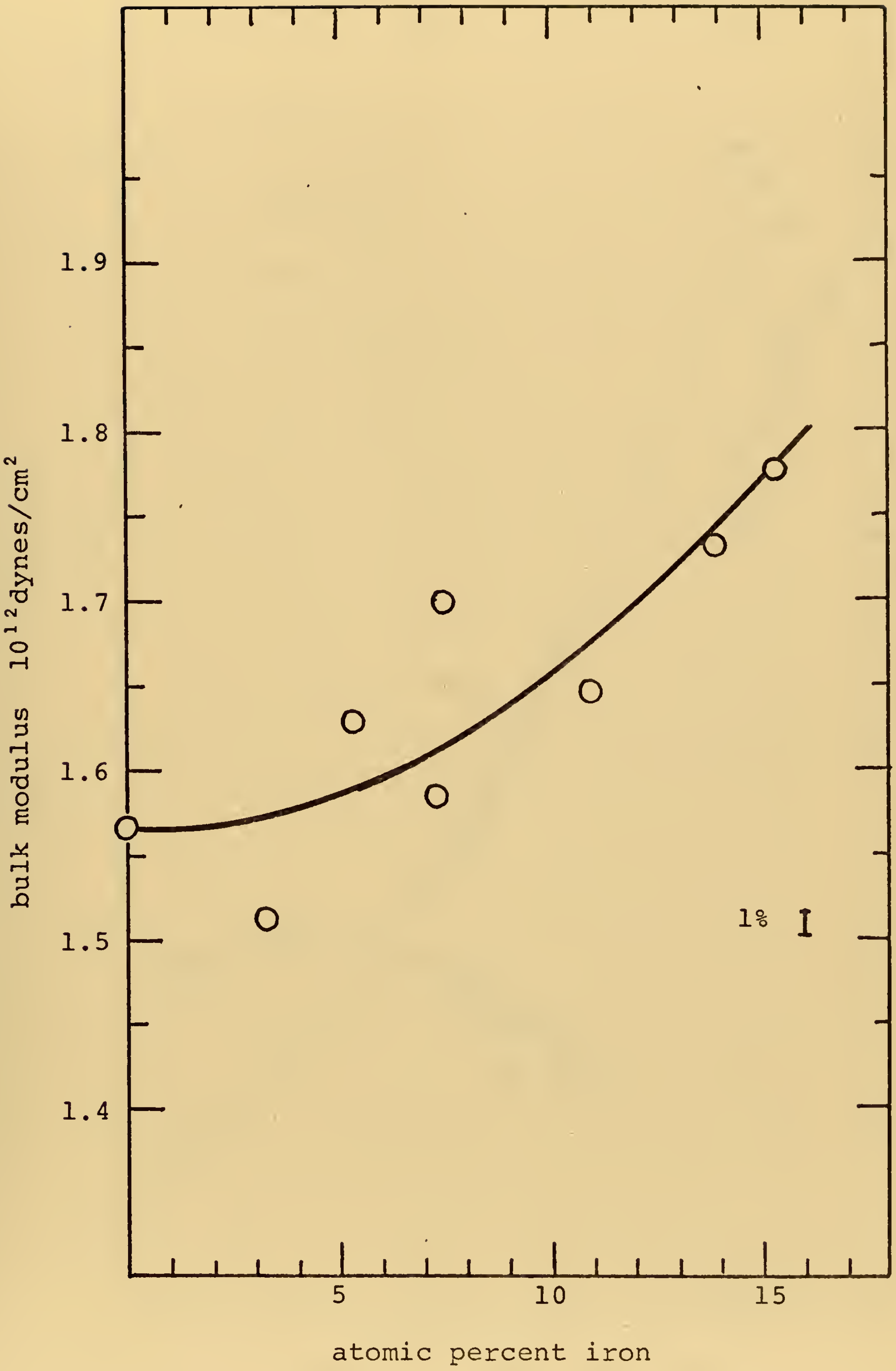

bulk modulus 10^{12}dynes/cm^2
1.9
1.8
1.7
1.6
1.5
1.4
1%
5
10
15
atomic percent iron

Figure 5

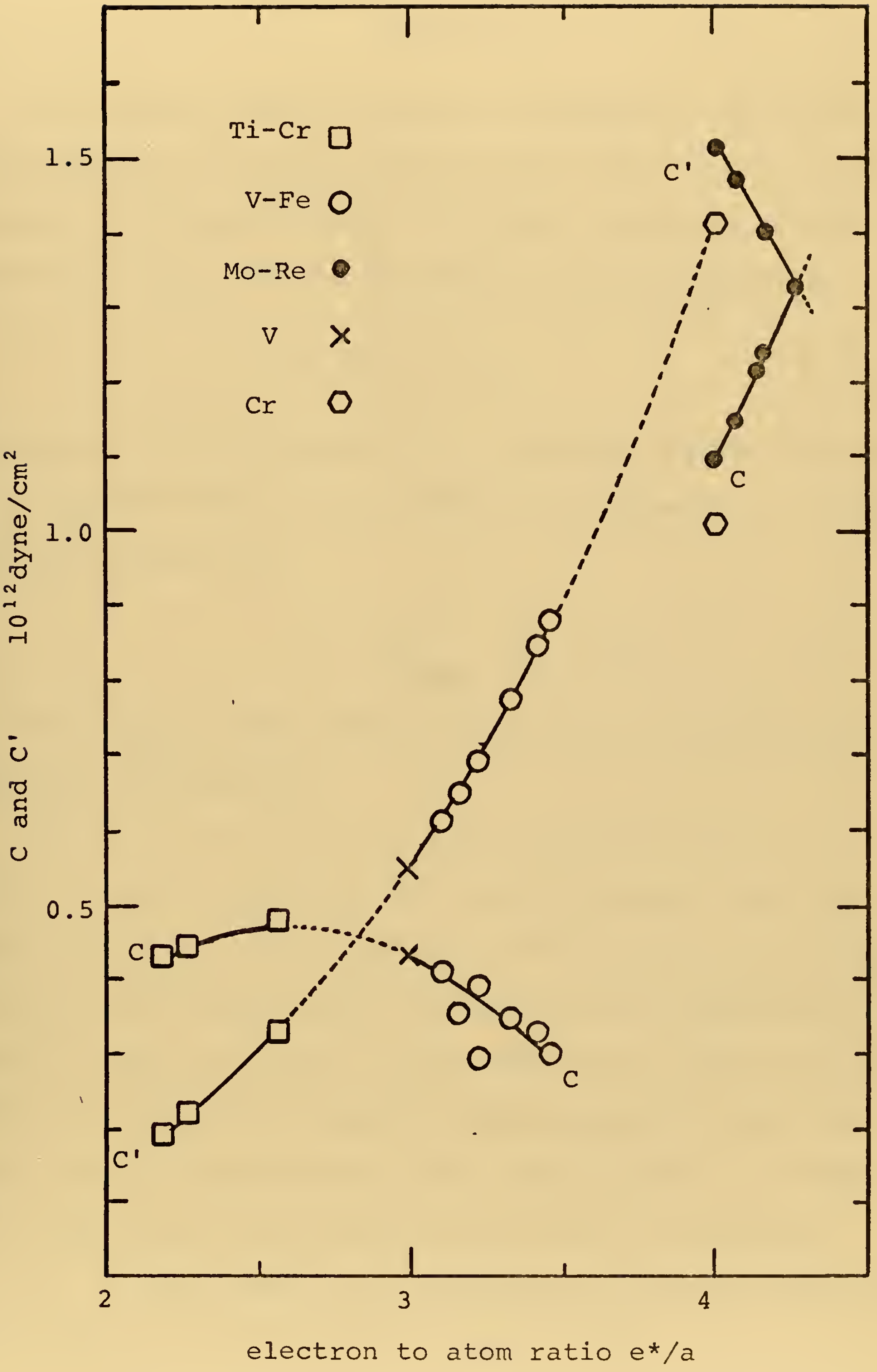

Ti-Cr □
V-Fe ○
Mo-Re ●
V ×
Cr ⬡
C and C' 10^{12}dyne/cm^2
1.5
1.0
0.5
C'
C
C
C'
C
2
3
4
electron to atom ratio e*/a

Figure 6

APPENDIX I

The elastic theory of solids is based on the Hooke's Law assumption that for sufficiently small strains, e_j, stress, T_i is proportional to strain, where the elastic constants, C_{ij}, are the constants of proportionality.

$$T_i = \sum_{j=1}^{6} c_{ij} e_j \qquad \text{A1.1}$$

Deformation of the medium in an adiabatic manner results in a stored elastic energy density, expressed by a strain-energy function, w.

$$w = \frac{1}{2} \sum_{j=1}^{6} \sum_{j=1}^{6} C_{ij}\, e_i\, e_j \qquad \text{A1.2}$$

In this notation the relation between i or j and the co-ordinate direction is

1 = xx 2 = yy 3 = zz 4 = yz 5 = zx 6 = xy

Here 1, 2 and 3 represent the normal strains which are those resulting from a stress on the face of a cube normal to the x axis and in the x direction etc. The numbers 4, 5 and 6 denote the shear strains which are those resulting from a stress on the face of a cube normal to the y axis and in the z direction etc. The shear strains in terms of infinitesimal displacements are given in equation A1.15. In both cases the summations on i and j allow for the general case of an anisotropic medium.

In terms of the energy density and/or the stress the constants of proportionality, C_{ij}, called the elastic constants, stiffness constants, or moduli of elasticity are

$$C_{ij} = \frac{\partial T_i}{\partial e_j} = \frac{\partial^2 w}{\partial e_i \, \partial e_j}\Big|_{e=o} \qquad (A1.3)$$

It is sometimes convenient to express relationships in terms of the reciprocal of the set of equations (A1.1).

$$e_i = \sum_{j=1}^{6} S_{ij} \, T_j \qquad (A1.4)$$

The coefficients of this set of equations, S_{ij}, are called the moduli of compliance. Treated as matrices the product matrix of the $[S_{ij}]$ and $[C_{ij}]$ array is the unit matrix, $[S_{ij}] \, [C_{ij}] = I$.

The strain-energy function, w, is the work done per unit volume in deforming the crystal and thus has the dimensions of erg-cm^3. The strains, e_j are dimensionless, thus the elastic constants also have the dimensions of an energy density usually expressed as dyne-cm^{-2}. In this work it has been convenient to show the C_{ij} in units of 10^{12} dyne-cm^{-2}.

The number of independent elastic constants is not 36 as equation (A1.2) might imply. From equation (A1.3) and the fact that δw is a perfect differential we see that

$$C_{ij} = \frac{\partial T_i}{\partial e_j} = \frac{\partial^2 w}{\partial e_i \partial e_j} = \frac{\partial^2 w}{\partial e_j \partial e_i} = \frac{\partial T_j}{\partial e_i} = C_{ji} \qquad (A1.5)$$

This symmetry $C_{ij}=C_{ji}$ reduces the maximum number of independent elastic constants to 21. The elastic constants are usually shown in a 6 by 6 array which for the most general case is

$$\begin{vmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{vmatrix} \qquad (A1.6)$$

The number of non-zero independent elastic constants is further reduced, except for the triclinic lattice, by the effect of lattice point symmetry operations. This effect can be demonstrated by writing down the strain-energy function in an original coordinate system and one obtained from the original by a lattice symmetry operation. If the two strain-energy functions are equated and coefficients of like strains compared the results are that certain constants become zero and others equal. For the particular case of cubic symmetry only 3 constants remain C_{11}, C_{12}, and C_{44}. Thus the array (A1.6) becomes

$$\begin{vmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{vmatrix} \qquad (A1.7)$$

Using this array we can write out equation (A1.2) for the strain-energy function in a cubic crystal.

$$w = \frac{1}{2} C_{11}[e_1^2+e_2^2+e_3^2]+C_{12}[e_1 e_2+e_2 e_3+e_3 e_1]+\frac{1}{2}C_{44}[e_4^2+e_5^2+e_6^2] \qquad (A1.8)$$

A direct application of equation (A1.3) defines the cubic elastic constants ie $C = \frac{\partial^2 w}{\partial e_1^2}$ etc. It is often more convenient when dealing with theories that derive the elastic constants from fundamental concepts to define certain combinations of the constants C_{11}, C_{12} and C_{44}. An equivalent set of these constants are

$$\begin{aligned} C' &= 1/2\ (C_{11}-C_{12}) \\ C &= C_{44} \\ B &= 1/3(C_{11}+ 2\ C_{12}) \end{aligned} \qquad (A1.9)$$

In this set the constants C and C' are shear constants chosen because they can be obtained from the strain energy function by strains that preserve the volume of the unit cell to first order in the e_i. The constant B, is the

bulk modulus and is the elastic constant corresponding to hydrostatic compression. These three cases are obtained from the cubic strain-energy function (A1.8) by choice of the appropriate strains.

1. $C' = 1/2(C_{11}-C_{12})$. In this case the cube is compressed along one axis and extended along a second so that two of the strains, say, e_1 and e_2 are equal in magnitude but opposite in sign. All other strains are zero. Then equation (A1.8) becomes

$$w = (C_{11}-C_{12})e_1^2 \qquad \text{from which}$$

$$C' = \frac{1}{4}\frac{\partial^2 w}{\partial e_1^2}\bigg|_{e_1 = 0} \qquad \text{(A1.10)}$$

2. $C = C_{44}$. This corresponds to shear in a plane parallel to a cubeface so that one strain, say e_4 is finite and all others are zero. Then equation (A1.8) becomes

$$w = C_{44}e_4^2 \qquad \text{from which}$$

$$C_{44} = \frac{\partial^2 w}{\partial e_4^2}\bigg|_{e_4 = 0} \qquad \text{(A1.11)}$$

3. $B = 1/3(C_{11} + 2\,C_{12})$ For the case of hydrostatic compression the three normal strains are equal and negative and the three shear strains are zero. Then equations (A1.8) becomes

$$w = \frac{3}{2}\,[C_{11}+ 2C_{12}]e_1^2 \qquad \text{from which}$$

$$B = \frac{1}{9}\frac{\partial^2 w}{\partial e_1^2}\bigg|_{e_1 = 0} \qquad \text{(A1.12)}$$

A cubic crystal is said to be isotropic if the two shear constants in equation (A1.9) are equal. The ratio of these constants, A = C/C' is called the anisotropy and for an isotropic crystal A=1. Thus, the effect is to reduce the number of non-zero independent elastic constants to two. These are generally chosen to be $C_{44} = \mu$ and $C_{12} = \lambda$. The constants λ and μ are called the Lame' constants. The elastic constant C_{11} then maybe written in terms of the Lame' constants and the elastic constant array (A1.7) contains only two independent constants.

$$\left|\begin{array}{cccccc} (\lambda+2\mu) & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & (\lambda+2\mu) & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & (\lambda+2\mu) & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{array}\right| \qquad \text{(A1.13)}$$

Using equation (A1.1) the isotropic stress-strain relations may now be written out.

$$\begin{aligned} T_1 &= (\lambda+2\mu)e_1+ \lambda(e_2+e_3) = \lambda\Delta+2\mu e_1 \\ T_2 &= (\lambda+2\mu)e_2+ \lambda(e_1+e_3) = \lambda\Delta+2\mu e_2 \\ T_3 &= (\lambda+2\mu)e_3+ \lambda(e_2+e_1) = \lambda\Delta+2\mu e_3 \\ T_4 &= \mu e_4 \\ T_5 &= \mu e_5 \\ T_6 &= \mu e_6 \end{aligned} \qquad \text{(A1.14)}$$

Here $\Delta = e_1+e_2+e_3$ is called the dilatation. Following Mason [Ref. 15] the expressions for the transmission of sound waves in isotropic solids may now be readily developed.

In terms of infinitesimal particle displacements u, v, and w in the x, y and z directions respectively the strains are:

$$e_1 = \frac{\partial u}{\partial x} \qquad e_2 = \frac{\partial v}{\partial y} \qquad e_3 = \frac{\partial w}{\partial z} \qquad \text{(A1.15)}$$

$$e_4 = \left(\frac{\partial v}{\partial z} - \frac{\partial w}{\partial y}\right) \quad e_5 = \left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}\right) \quad e_6 = \left(\frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}\right)$$

The equation of motion of an infinitesimal volume element of density in the x direction is

$$\rho \frac{\partial^2 u}{\partial t^2}\, dx\, dy\, dz = F_x \qquad \text{(A1.16)}$$

and similarly for y and z. The force F_x is that arising from a stress $-T_1(x)$ on the face at x of a cube of volume $\Delta x \Delta y \Delta z$ and a stress $T_1(x+\Delta x) = T_1(x) + \frac{\partial T}{\partial x}\Delta x$ on the face at $(x+\Delta x)$. Other forces in the x direction arise from the shear stresses T_5 and T_6 so that in equation (A1.16)

$$F_x = \left[\frac{\partial T_1}{\partial x} + \frac{\partial T_6}{\partial y} + \frac{\partial T_5}{\partial z}\right] dx\, dy\, dz \qquad \text{(A1.17)}$$

and similarly for F_y and F_z.

If one substitutes for the e_i in equation (A1.14) equation (A1.15) and take the derivatives indicated by equation (A1.17) the equations of motion (A1.16) become

$$\rho \frac{\partial^2 u}{\partial t^2} = (\lambda+2\mu) \frac{\partial \Delta}{\partial x} + \mu\nabla^2 u$$

$$\rho \frac{\partial^2 v}{\partial t^2} = (\lambda+2\mu) \frac{\partial \Delta}{\partial y} + \mu\nabla^2 v \qquad \text{(A1.18)}$$

$$\rho \frac{\partial^2 w}{\partial t^2} = (\lambda+2\mu) \frac{\partial \Delta}{\partial z} + \mu\nabla^2 w$$

where $\nabla^2 = (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$.

If the three equations (A1.18) are differentiated with respect to x, y and z respectively and the resulting equations summed, a wave equation for the dilatation is obtained

$$\rho \frac{\partial^2 \Delta}{\partial t^2} = (\lambda+2\mu)\nabla^2\Delta \qquad \text{(A1.19)}$$

For a plane wave, with particle motion u only, equation (A1.19) becomes

$$\rho \frac{\partial^2 u}{\partial t^2} = (\lambda+2\mu) \frac{\partial^2 u}{\partial x^2} \qquad \text{(A1.20)}$$

which shows the velocity of a longitudinal wave traveling in the x direction to be

$$V_L = \sqrt{\frac{\lambda+2\mu}{\rho}} \qquad \text{(A1.21)}$$

To obtain a transverse wave equation the first and third of equation (A1.18) are differentiated with respect to z and x respectively and the difference is formed.

$$\rho \frac{\partial^2}{\partial t^2} [\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}] = \mu\nabla^2 [\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}] \qquad \text{(A1.22)}$$

Then assuming a transverse plane wave traveling in the z direction with particle motion in the u direction,

$u = e^{i(kz-\omega t)}$ equation (22) becomes

$$\rho \frac{\partial^2 u}{\partial t^2} = \mu \frac{\partial^2 u}{\partial z^2} \tag{A1.23}$$

from which the transverse wave velocity is

$$V_s = \sqrt{\frac{\mu}{\rho}} \tag{A1.24}$$

Finally, in the discussion of polycrystalline materials whose isotropy results from the random orientation of generally anisotropic crystallites the shear constant has been called G. Setting G equal to μ and using the definition of the bulk modulus along with the Lame' constants

$$(\lambda+2\mu) = (B + \frac{4}{3} G) \tag{A1.25}$$

Substituting into (A1.21) and (A1.24) the polycrystalline cubic material velocity equations become

$$\begin{aligned} V_L &= \sqrt{\frac{B+\frac{4}{3}G}{\rho}} \\ V_s &= \sqrt{\frac{G}{\rho}} \end{aligned} \tag{A1.26}$$

APPENDIX II

The treatment of elasticity in Appendix I is based on a classical Hooke's Law force and its attendent strain-energy function. In calculating the elastic constants from fundamental consideration one must generate a function U which is the total energy per atom. The equivilance of this function and the strain-energy function, w, is assumed so that in terms of the energy, U, the definition of the elastic constants is

$$C_{ij} = \frac{\partial^2 U}{\partial e_i \partial e_j}\bigg|_{e=o} \qquad \text{(A2.1)}$$

The total energy is a sum of contributions arising from the various forces between atoms in solids.

A successful theory of U which is a function of the interatomic spacing will give first, the cohesive energy of the crystal and secondly upon differention, the equilibrium lattice constant. Thirdly, another differentiation of U as in (A2.1) will give the elastic constants. This latter requirement is a rigorous test of the validity of any fundamental theory of the total energy.

Present day theories of the total energy U, which have been applied to the determination of the elastic shear constants C and C', originated with Fuchs. Fuchs applied the methods of Wigner and Seitz for determining the cohesive energy of metalic sodium. He extended the treatment to

copper, and later calculated the elastic constants of copper [Ref. 1].

Fuch's calculation was applied to transition elements by Zener [Ref. 16] and Isenberg [Ref. 17]. They concluded that the observed stability of the bcc transition elements resulted largely from a repulsive interaction between second nearest neighbors arranged in a anti-ferromagnetic array. Neighbors and Smith use Fuch's calculation to discuss dilute alloying of other elements with copper [Ref. 18].

It is instructive to consider the calculation of Wigner and Seitz for the cohesive energy of metalic sodium since the contributions to the total energy for this case can be extended to other monovalent metals.

The electronic configuration of sodium is a single s electron outside of a closed neon core. In the solid state this electron is assumed to be free to move through the crystal lattice and Wigner and Seitz calculate the energy of the lowest state, U_o, of the free electron. The calculation is facilitated by imagining the lattice to be divided into polyhedra constructed by erecting planes which are perpendicular bisectors of the lines joining an atom to its neighbors. Such polyhedra are adjacent and fill all space occupied by the lattice. The motion of the electron through the lattice then becomes a motion between adjacent identical polyhedra. Such a motion will be periodic with respect to the dimensions of the polyhedra and the boundary conditions on the electron wave function will be

that the function be continuous between polyhedra and that it approach the zone boundary normally. On the average a monovalent metal will have only one electron per polyhedron. This is a result of both Coulomb repulsion and the effects of the Pauli exclusion principle. Thus each electron finds itself at a given instant confined to a atomic polyhedron influenced by the potential of the central ion core. Wigner and Seitz assumed a potential by Prokofjew [Ref. 19] to calculate the wave function and U_o, the lowest state energy of this one electron system.

Since the atomic polyhedron is not very different from a sphere, they assumed that it may be replaced by a sphere of equal volume. The radius of this sphere is r_o, defined by $\frac{4}{3}\pi r_o{}^3=\Omega$ where Ω is the atomic volume.

The radial wave function $R = r\Psi(r)$ so that the boundary condition on Ψ which is $\frac{\partial\Psi}{\partial r}\Big|_{r=r_o} = 0$ becomes

$$\frac{\partial R}{\partial r}\Big|_{r=r_o} = \frac{R}{r} \qquad \text{(A2.2)}$$

A convenient way to obtain the dependence of the energy on the radius of the sphere is to solve the radial Schrodinger equation for the wave function at arbitrary energies U_o. After obtaining the wave function, $R(r)$, a tangent drawn from the origin to the curve will satisfy the boundary condition (A2.2) at two radii. Thus from each radial function two points on the $U(r)$ curve are determined. Calculation of several radial function allows the $U(r)$ curve to be mapped out. For sodium such a curve has a minimum and the

lattice would be stable without considering other contributions to the energy.

In fact however, the electrons in the metal are distributed over states above U_o, the energy of the lowest state, by the Fermi distribution function. Thus to the energy of the lowest state must be added the average additional electron kinetic energy. This energy is determined from the fermi energy

$$U_F = \frac{\hbar^2}{2m} \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r^2} \tag{A2.3}$$

where the average kinetic energy of an electron is

$$\overline{U}_F = \frac{3}{5} U_F \tag{A2.4}$$

These are the primary contributions to the cohesive energy of sodium. However, sodium has a relatively small ion core size so that the increase in the energy of the lattice from core overlap forces is not significant. The larger ion core size in copper does not allow this assumption and the repulsive exchange energy between ions must also be considered. This energy is usually assumed to have the form

$$U_I = \frac{SW}{2} \tag{A2.5}$$

where W is the repulsive bond energy of a single pair of ions and S is the lattice coordination number. W is usually taken to be of the form

$$W = De^{-r/\rho} \tag{A2.6}$$

Since ρ is a small fraction of the interatomic distance only first and second nearest neighbors are usually considered to take part in the interaction. Other energies which are small and do not contribute substantially to the cohesive energy are the Van der Waals energy and a correction to the lowest state energy. This correction U_L is the result of polyhedron-polyhedron interaction and is the sum of two terms.

$$U_L = U_E - U_S \tag{A2.7}$$

where U_E is the energy of a lattice of positive point charges immersed in a negative electron sea and U_S in the energy of a positive point charge in a sphere of negative charge.

The fact that a certain energy contributes significantly to the cohesive energy does not imply that it will significantly affect the elastic constants. In obtaining the elastic shear constants of copper from the energies outlined above Fuch's used only the coulomb attraction energy of U_E in equation (A2.7) and the overlap repulsion energy of equations (A2.5) and (A2.6).

The reasons the other energies do not contribute to the shear constants are as follows:

a) For the equilibrium lattice spacing $U_o(r)$ is close to an inflection point and its second derivative is close to zero.

b) For monovalent metals the Fermi surface is near the center of the Brillouin zone and is approximately spherical. Thus shear strains do not alter the average electron energy.

c) The Fermi energy and the spherical contribution to U_L, and U_S, are volume dependent energies. However, the strains chosen to define C and C' conserve the volume and thus these energies do not contribute to the to the elastic constants.

d) The Van der Waals energy makes only a minor contribution to C and C'.

Thus Fuch's retained only two contributions to the energy

$$U = U_I + U_E \tag{A2.8}$$

where U_E is the electrostatic potential energy of a lattice of point changes + e imbedded in a uniform negative change distribution of -e per atomic volume and the energy U_I is the exchange repulsion energy between closed shell ion cores.

For a bcc lattice U_E can be evaluated using the Ewald method [Ref. 20] to do the lattice sum and the electrostatic contributions to the elastic constants are then calculated using equation (A2.1) so that

$$C'_E = 0.0997 \frac{e^2}{a^4} \qquad C_E = 0.7423 \frac{e^2}{a^4} \tag{A2.9}$$

where a is the lattice constant.

Similarily ionic stiffnesses C'_I and C_I are given by Fuch's in terms of the energy W of equation (A2.6)

$$C'_I = \frac{4}{3}N\,[rW'_1]_1 + \frac{1}{2}N\,[r^2W''_2]_2 + \frac{1}{2}N\,[rW'_2]_2$$

$$C_I = \frac{4}{9}N\,[r^2W''_1]_1 + \frac{8}{9}N\,[rW'_1]_1 + N\,[rW'_2]_2 \qquad \text{(A2.10)}$$

Here allowance has been made that the nearest neighbor interaction W_1 may differ from the next nearest neighbor interaction W_2 Primes indicate differentiation and the subscripts on the brackets denote evaluation at a distance r between ions corresponding to first or second nearest neighbors.

The total shear constants are then

$$C = C_I + C_E \qquad C' = C'_I + C'_E \qquad \text{(A2.11)}$$

In practice C_I and C'_I are usually determined by calculating C_E and C'_E and subtracting this from the measured constants. Featherston and Neighbours [Ref. 21] have done this for V, Nb, Ta, Mo, W and Fe. They note, in agreement with Isenberg, that for all cases except Fe the term $\frac{4}{3}N(rW'_1)_1$ in C'_I is negative and so must be offset by the second nearest neighbors.

The application of this analysis to dilute alloys of copper was done by Neighbors and Smith. By introducing parameters to accomodate the effects of solute atoms on the electron to atom ratio and the ionic overlap contribution and by correcting for changes in the stiffnesses due

to changes in the lattice constant with solute they calculate corrections to C and C'.

Further extensions of Fuch's theory to the transition elements and their alloys has encountered the difficulty of dealing with the status of the d-electrons. Such electrons are more tightly bound than s electrons, they thus occupy a relatively narrow band with a correspondingly higher density of states than s electrons. Further, the d wave functions are more directional in character. The multi-valency of these metals and the changes in e/a with alloying will certainly cause changes in the fermi surface which could result in an electron gas contribution to the shear constants. The antiferromagnetic array that Zener and Isenberg predicted using Fuch's work has only been observed experimentally for chromium.

REFERENCES

1. K. Fuchs, Proceedings of the Royal Society 151,585 (1935)

2. W. B. Pearson, Lattice Spacings and the Structure of Metals and Alloys, Permagon Press 1967, Vol 2, 943

3. R. Hill, Proceedings of the Physical Society (London) A65, 349, (1952)

4. G.A. Alers, Physical Review, 119, 1532 (1960)

5. E.S. Fisher and D. Dever, Acta Metullurgica 18,265 (1970)

6. W. Voigt, "Lehrbuch der Kristalphysik" pp 716-761 Teubner, Leipzig, (1928)

7. A. Reuss. Z. Angew Math. Mech. 9,55 (1929)

8. E.C. Snow and J.T. Waber, Acta Metullurgica 17,623 (1969)

9. D.L. Davidson and F.R. Brotzen, Journal of Applied Physics 39,5768 (1968)

10. E.O. Hall and S.H. Algie, Metallurgical Reviews 11, 61 (1966)

11. G. Simmons and H. Wang, Single Crystal Elastic Constants and Calculated Aggregate Properties, A Handbook, MIT Press 1971

12. R.W. Huber, NRL Report No. 5928 April 1963

13. K.P.V. Lei and T.A. Sullivan, Journal of Less Common Metals, 14,145 (1968)

14. W.E. Anable, Journal of Vacuum Science and Technology, 7,S74 (1970)

15. W.P. Mason, Physical Acoustics, Van Nostrand (1958) p. 12.

16. C. Zener, Physical Review 81,440 (1951)

17. I. Isenberg, Physical Review, 83,637 (1951)

18. J.R. Neighbours, and Charles S. Smith, Acta Mettallurgica, 2,591, (1954)

19. W. Prokofjew, Zeit. fur Physik, 58,255, (1929)

20. J.M. Ziman, "Principles of the Theory of Solids" Cambridge University Press (1964) pp 39

21. F.H. Featherston and J.R. Neighbours Physical Review 130, 1324 (1963)

INITIAL DISTRIBUTION LIST

No. Copies

1. Defense Documentation Center 2
Cameron Station
Alexandria, Virginia 22314

2. Library, Code 0212 2
Naval Postgraduate School
Monterey, California 93940

3. Professor J. R. Neighbours, Code 61 1
Department of Physics
Naval Postgraduate School
Monterey, California 93940

4. Professor E. C. Crittenden, Jr. 1
Department of Physics
Naval Postgraduate School
Monterey, California 93940

5. LCDR John J. Donegan, Jr. 1
62 West Lake Road
Trumbull, Connecticut 06611

6. Commander Naval Facilities 1
Engineering Command
Washington, D.C. 20390
Attn: Mr. Herbert C. Lamb, Code 0322

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Postgraduate School Monterey, California 93940	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Elastic Constants of Polycrystalline Vanadium-Iron Alloys

4. DESCRIPTIVE NOTES *(Type of report and, inclusive dates)*

Doctor of Philosophy, September 1972

5. AUTHOR(S) *(First name, middle initial, last name)*

John Joseph Donegan, Jr.

6. REPORT DATE September 1972	7a. TOTAL NO. OF PAGES 60	7b. NO. OF REFS 21

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Naval Postgraduate School Monterey, California 93940

13. ABSTRACT

Polycrystalline alloys of iron in vanadium up to 15.32 atomic percent were prepared principally by arc melting. In order to obtain the elastic constants and investigate the possibility of the existence of an elastically isotopic alloy ultrasonic measurements were made. These measurements determined the longitudinal and transverse wave velocities in the 10-30 MHz range at room temperature. The resulting longitudinal modulus increased with alloying whereas the shear modulus remained roughly constant although the data are somewhat scattered. These data are interpreted to show that the shear constants vary through alloying in a manner consistent with the results of other experiments and that the results are consistent with a $s^1 d^{n+1}$ electronic configuration in the transition metals. The existence of an isotropic alloy is indicated for alloys with electron to atom ratios lower than vanadium rather than for the alloys measured.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6811

A-31408

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Vanadium						
Vanadium alloy						
Elastic constants						
Transition metal alloy						
Alloy electron distribution						